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(21) International Application Number: PCT/SE97/01060 (22) International Filing Date: 16 June 1997 (16.06.97) (30) Priority Data: 9602602-6 28 June 1996 (28.06.96) SE (71) Applicant (for all designated States except US): SUNDS DEFI- BRATOR INDUSTRIES AB [SE/SE]; S-851 94 Sundsvall (SE). (72) Inventors; and (75) Inventors/Applicants (for US only): BOMAN, Rolf [SE/SE]; Idrottsgatan 17, S-856 43 Sundsvall (SE). BOKSTRÖM, Monica [SE/SE]; Bjärne 3251, S-860 25 Kovland (SE). GERMGÅRD, Ulf [SE/SE]; Mastvägen 5, S-865 31 Alnö (SE). MELLANDER, Pia [SE/SE]; Flottiljvägen 4, S-865 32 Alnö (SE). NORDÉN, Solveig [SE/SE]; Odalvägen 14, S-862 41 Njurunda (SE). SUNDIN, Matts [SE/SE]; Skonertvägen 14, S-865 32 Alnö (SE). (74) Agent: IVENSEN HASSELROT, Eva; L.A. Groth & Co. KB, P.O. Box 6107, S-102 32 Stockholm (SE).		(81) Designated States: AU, BR, CA, CN, JP, NO, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PRESSURIZED CHLORINE DIOXIDE BLEACHING WITH RECOVERY OF CHLORINE DIOXIDE (57) Abstract The present invention relates to a multi-stage paper pulp bleaching process in which at least one of the bleaching stages is carried out in a reactor with chlorine dioxide at a pulp concentration of 8-40 %. The pulp is bleached with chlorine dioxide in a pressurized vessel at an overpressure of 0.1-10 bars and at a temperature of between 90-110 °C and for a reaction time of 1-90 minutes. The pressure of the pulp is lowered in a downstream tower in a manner such as to also lower the temperature of the pulp and enable residues of chlorine dioxide to be extracted in gas phase.		

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PRESSURIZED CHLORINE DIOXIDE BLEACHING WITH RECOVERY OF CHLORINE DIOXIDE

The present invention relates to a method of bleaching paper pulp with chlorine dioxide in a plurality of stages of which at least one stage is a chlorine dioxide stage.

Modern paper pulp bleaching methods are based on the use of chlorine dioxide (D) as the main bleaching chemical. The bleaching methods often comprise several stages, and the chlorine dioxide bleaching effect is enhanced by also including an oxygen gas stage (O) and/or a hydrogen peroxide stage (P) in the bleaching sequence, such as sequences of the type OP(EPO)DD, where (E) stands for extraction. The pulp is bleached to a high degree of purity by these bleaching methods in a manner which is gentle on the pulp. The load on the environment is also low, since the concentrations of, e.g., AOX, chlorinated phenols, chlorinated dioxins, etc., have been limited by said methods.

Because it has been possible to lower the kappa number as a result of improved pulp digestion and oxygen-gas delignification technology, the need for bleaching chemicals has diminished. In spite of this, the majority of bleaching sequences still require from four to five bleaching stages, due to the fact that the terminating bleaching process is carried out under conditions that cause the reaction mechanisms to take place slowly and ineffectively. In traditional bleaching departments, the pulp is bleached in from five to six bleaching stages in accordance with the aforesaid type of sequence, despite the bleaching requirement being from two to four times greater than in the most modern of present-day pulp mills.

Known chlorine dioxide bleaching processes are comprised of sequences in which the chlorine dioxide stages are carried out at pulp concentrations of about 10-15%. When bleaching is carried

out in a pre-bleaching stage, the temperature is between 20-60°C at pH 2-3 over a reaction time of 0.5-1 hour. When bleaching is carried out in a final bleaching stage, the temperature is higher, about 50-80°C, at pH 4-5, although the reaction time is longer, from 2-4 hours.

Bleaching at higher temperatures in order to shorten the reaction time cannot be readily effected, however, on a full scale. It is necessary to carry out the bleaching process in a pressurized reactor instead of in a conventional bleaching tower. When the pressure is dropped, chlorine dioxide gas residues that are harmful to the health are given off. Pulp that contains residual chlorine/residual chlorides cannot be readily passed to a subsequent wash without being cooled, since the wash environment would otherwise become much too corrosive.

The object of the present invention is to solve the aforesaid problems so that the desired bleaching result can be achieved at lower costs.

The characteristic features of the invention will be apparent from the following Claims.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates preferably to the bleaching of paper pulp with chlorine dioxide. The pulp is bleached in several stages, of which at least one stage is a chlorine dioxide stage. The pulp shall have a concentration of 8-40%, preferably 10-15%. The chlorine dioxide bleaching process is carried out in a pressurized reactor at an overpressure of 0.1-10 bars at a temperature of 90-110°C and with a reaction time of 1-90 minutes, preferably 15-30 minutes. Subsequent to treatment with chlorine dioxide, the pulp is transferred to a downstream tower in which

the pressure is lowered, wherein the temperature of the pulp also falls and residues of gaseous chlorine dioxide are released, these residues later being removed with cold water. The water containing chlorine dioxide is recycled to the reactor, where it is charged to the chlorine dioxide stage together with dilution water and additional chlorine dioxide.

The pulp from which gaseous chlorine dioxide has been removed is cooled further by delivering SO_2 -containing water to the bottom of the downstream tower on the suction side of the pump. The pulp is cooled to a temperature that shall not exceed 80°C , whereafter the pulp is pumped to a downstream washing stage. The addition of the SO_2 -containing water enables further residual chlorine in the pulp to be eliminated.

The invention will be described hereinafter with reference to an exemplifying embodiment thereof.

The pulp to be bleached is paper pulp, for instance sulphite pulp or sulphate pulp.

Example

Sulphate pulp/sulphite pulp having a pulp concentration of between 10-15% was treated with chlorine dioxide in a pressurized reactor. The pulp was treated for 15-30 min. at a temperature of about $90-110^\circ\text{C}$. After treatment with chlorine dioxide, the pulp was transported to a downstream tower in which the temperature was lowered and chlorine dioxide residues were extracted in gas phase, whereafter the pulp was cooled to 80°C by adding SO_2 -containing water to eliminate residual chlorine in the pulp.

Bleaching can be effected more quickly and more effectively, by bleaching with chlorine dioxide at a higher temperature. The

shorter reaction time in the pressurized vessel enabled the bleaching equipment to be reduced, thereby enabling the costs entailed by ground area and building volume to be also reduced. This represents a considerable reduction in the cost of bleaching paper pulp.

Other advantages afforded by the inventive method include the recirculation of chlorine dioxide, which enables the burden of chlorine-containing compounds on the environment to be minimized or completely eliminated.

CLAIMS

1. A method of bleaching paper pulp in a plurality of stages of which at least one of the bleaching stages is carried out in a pressurized vessel with chlorine dioxide at a temperature of between 90-110°C and at an overpressure of 0.1-10 bars during a reaction time of 1-90 minutes and at a pulp concentration of 8-40%, preferably 10-15%, characterized by lowering the pressure of the pulp in a downstream tower in a manner such as to also lower the temperature of the pulp and enable chlorine dioxide residues to be extracted in a gas phase, extracting chlorine dioxide from the gas phase with the aid of cold water, and recycling the chlorine-dioxide containing water from the extraction of chlorine dioxide to the reactor together with dilution water, which is charged to the chlorine dioxide stage.

2. A method according to Claim 1, characterized in that the reaction time of the chlorine dioxide bleaching process is 15-30 minutes.

3. A method according to Claim 1 or 2, characterized by further cooling the pulp with SO₂-containing water charged to the bottom of the downstream tower, and eliminating residual chlorine present in the pulp.

4. A method according to any one of Claims 1-3, characterized by colloing the SO₂-containing water before charging the water to the pulp.

5. A method according to any one of Claims 1-4, characterized in that the pulp that is pumped to the following washing stage has a temperature of $\leq 80^{\circ}\text{C}$.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/01060

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SE 9303037-7 A (SUNDS DEFIBRATOR INDUSTRIES AB), 17 March 1995 (17.03.95) --	1-5
A	US 2706673 A (E.R.BURLING ET AL), 19 April 1955 (19.04.55) -----	1-5

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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SE 9303037-7 A	17/03/95	NONE	
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US 2706673 A	19/04/55	NONE	
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